

The Formation of hematite from ferrihydrite using Fe(II) as a catalyst

Hui Liu^{a,b}, Yu Wei^{b,*}, Yuhan Sun^a

^a Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

^b College of Chemistry, Hebei Normal University, Hebei Province, Shijiazhuang 050016, China

Received 13 July 2004; received in revised form 16 September 2004; accepted 18 September 2004

Available online 11 November 2004

Abstract

The objective of the research is to determine the effects of Fe(II) on the phase transformation from ferrihydrite to hematite in pH range 5–9 at 100 °C. It is confirmed that Fe(II) is a catalyst in the process of phase transformation of ferrihydrite. On one hand, Fe(II) can catalyze the formation of hematite by a dissolution/reprecipitation mechanism. On the other hand, Fe(II) can catalyze the formation of hematite by a solid-state transformation. The species of Fe(II) that take catalytic action on the phase transformation of ferrihydrite are probably FeOH⁺ and Fe(OH)₂. Both dissolution/reprecipitation and solid-state transformation can be explained by electron transfer. This phase transformation from ferrihydrite to hematite, which is called as catalytic phase transformation, can be employed to synthesize hematite particles rapidly. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ferrihydrite; Fe(II); Catalytic phase transformation; Hematite; Formation mechanism

1. Introduction

Iron(III)-oxyhydroxides and oxides can be produced from aqueous solution using different experimental routes, such as forced hydrolysis of iron salts and crystallization from iron(III)-hydroxide gel, etc. Music et al. [1] studied the formation of a solid phase during the hydrolysis of various iron(III)-salt solutions and on the basis of the experimental results a mechanism for the precipitation by the forced hydrolysis of acidic iron(III)-salt solutions was proposed. Sugimoto et al. [2] investigated in detail the phase transformation from ferric hydroxide gel into pseudocubic α -Fe₂O₃ particles. They found that the α -Fe₂O₃ particles were actually formed through a distinct two-step phase transformation from Fe(OH)₃ to β -FeOOH and from β -FeOOH to α -Fe₂O₃. Each unit process proceeded through the deposition of the solute with the dissolution of each precursory solid.

Ferrihydrite is often used as the precursor to synthesize hematite. The data reported by Schwertmann et al. [3] indicate that two-line ferrihydrite kept under water at tempera-

tures of 4–30 °C and at pH of 2–12 transformed into goethite and/or hematite. With higher temperature hematite was favored and the strong hematite favoring effect appeared at pH values close to the point of zero charge (pzc) of ferrihydrite. There are also some data in the literature concerning the effects of various additives, such as organic acid, silicates, Al, Mn, Ti, Cu, etc. on the process of ferrihydrite phase crystallization [4,5]. Cornell and Pflanzenernahr [6] classified the effects of some additives, such as simple ions and molecules on the phase transformation of ferrihydrite. Some additives, e.g. oxalate and L-tartarate, can promote the formation of hematite from ferrihydrite. Lactate retards the formation of goethite and L-cystine can cause a rapid phase transformation from iron(III)-hydroxide to α -FeOOH [7].

In addition to the above additives, some investigators have paid attention to the effect of Fe(II) ions on the phase transformation of iron(III) (hydro)oxides. Wehrli et al. [8] have studied the Fe(II)-catalyzed reductive dissolution of iron(III) (hydro)oxides and attempted to provide some mechanistic insight into the catalysis of redox reactions at hydrous oxide surfaces. Other investigators have reported that Fe(II) ions were adsorbed onto amorphous ferric oxide (AFO) to form a more stable phase in alkaline medium [9,10].

* Corresponding author. Tel.: +86 0311 6268342; fax: +86 0311 5893425.
E-mail address: weiyu@mail.hebtu.edu.cn (Y. Wei).

Recently we found that Fe(II) adsorbed onto ferrihydrite can cause a rapid phase transformation from ferrihydrite to hematite at pH 5–9 at 100 °C. The action of Fe(II) was confirmed to be catalytic. One of the aims of the present work is to study the influence of Fe(II) on the ferrihydrite phase transformation into hematite in the near neutral pH medium. At the same time, we were also aiming to find some experimental evidence elucidating the mechanism of this transformation.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH) of analytical purity and distilled water were used. The ferric salt solutions were filtered through a 0.22 μm Millipore filter to remove any particulate contaminants before use.

2.2. Experimental

Prior to synthesis, pure nitrogen gas (99.99%) was passed through all solutions used, respectively, in order to remove dissolved oxygen gas. Ferrihydrite was prepared by the following procedures. NaOH solution (7.5 mol/L) was added into Fe(III) salt solution (50 ml, 1 mol/L) until pH 5–9 under the condition of vigorous stirring. When the pH of the system was adjusted to a desired pH, the agitation was continued for an additional 10 min followed by adding trace amounts of Fe(II) ions into the system. The pH of the system was adjusted to the pH once again with a dilute NaOH solution and at the same time the total volume of each system was adjusted to 100 ml. All stages of the preparation were carried out under nitrogen, using degassed distilled water. In this mixed system, a gel-like deposit formed. Then this slurry was heated, with nitrogen flowing within the vessel until it boiled. The suspension was kept boiling and refluxing for a certain time under vigorous stirring. The product was centrifuged and washed thoroughly with distilled water and then dried at about 70–80 °C.

X-ray diffraction (XRD) patterns were obtained with a Bruker diffractometer D8 ADVANCE using a Cu K α radiation. The concentrations of Fe(II) ions and total iron in solution were determined spectrophotometrically by using 1,10-phenanthroline [11]. The total iron concentration in solution was determined after reducing iron(III) ions to Fe(II) ions with hydroxylamine.

3. Results and discussion

3.1. XRD patterns of ferrihydrite prepared at various pH

When the iron(III)-salt solution is mixed with the NaOH solution, the gel forms. Though the ratio of OH/Fe is ap-

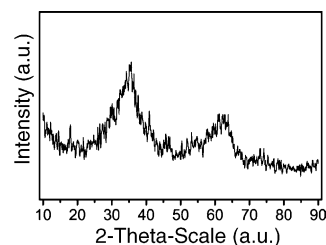


Fig. 1. XRD pattern of two-line ferrihydrite ($C_{\text{total Fe(III)}} = 0.5 \text{ mol/L}$, $\text{pH} = 7$).

proximately equal to 3, the product usually doesn't match the stoichiometry of $\text{Fe}(\text{OH})_3$. In our system, the product formed with NaOH solution added into Fe(III) solution until pH 5–9 was shown to be two-line ferrihydrite by XRD. The XRD pattern is shown in Fig. 1. Structurally, ferrihydrite is built from $\text{Fe}(\text{O}, \text{OH})_6$ octahedra sharing corners and edges, as deduced from EXAFS [12,13]. Two-line ferrihydrite forms by fast hydrolysis near pH 7 and shows two extremely broad XRD peaks at 0.25 and 0.15 nm which Feitknecht and Michaelis [14] attributed to hexagonally close-packed oxygen. Two-line ferrihydrite is a poorly ordered compound and it is, usually, stable at room temperature at neutral pH. With increasing temperature, it may transform to goethite and/or hematite depending on the physico-chemical conditions.

3.2. The times needed for completing the phase transformation from ferrihydrite to hematite in the presence or absence of Fe(II)

The times needed for completing the phase transformation from ferrihydrite to hematite particles both in the absence or presence of trace amounts of Fe(II) at 100 °C were determined. The results are shown in Fig. 2.

From Fig. 2 it can be seen that the times for completing the phase transformation in the absence of Fe(II) change with initial pH. When $\text{pH} < 4.5$, the times shorten with the increase of pH and the times prolong with the increase of pH when $4.5 < \text{pH} < 9.0$. When $\text{pH} > 9.0$, the phase transformation from ferrihydrite to hematite can be completed in a short time. The time–pH curve with small amounts Fe(II) in Fig. 2 indicates that the times for completing the phase transformation in the presence of Fe(II) ions become much shorter

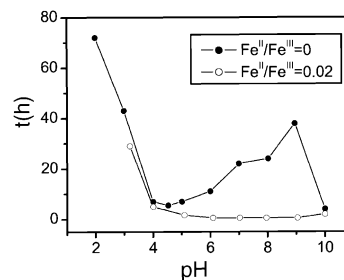


Fig. 2. The accelerating action of Fe(II) on the phase transformation of ferrihydrite ($C_{\text{total Fe(III)}} = 0.5 \text{ mol/L}$).

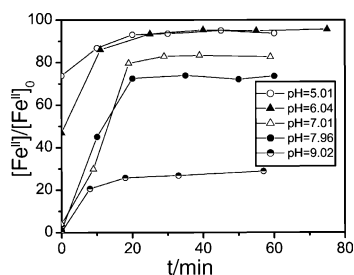


Fig. 3. The recovery curve of Fe(II) ions at different pHs ($C_{\text{total Fe(III)}} = 0.5 \text{ mol/L}$, $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.03$).

than those in the absence of Fe(II) ions. This phenomenon becomes more obvious especially in pH range 5–9. It implies that trace amounts of Fe(II) accelerate greatly the formation of $\alpha\text{-Fe}_2\text{O}_3$ particles in this pH range.

3.3. Determination of the recovery rate of Fe(II)

In order to understand the action of ferrous ions on the phase transformation of ferrihydrite, the concentration of Fe(II) ions desorbed into the solution at different reaction time was determined at various pHs under pure nitrogen (99.99%). The recovery curve of Fe(II) ions at different pHs were shown in Fig. 3.

From the result in Fig. 3, it is found that the recovery rate of Fe(II) decreases with the increase of pH. There are two reasons to explain this result. The first reason is that some of Fe(II) ions may be absorbed on the surface of $\alpha\text{-Fe}_2\text{O}_3$ particles because of their big specific surface area. The second reason may be that Fe(II) ions incorporate into the product to form an impurity phase. But its amount is too small to be determined by XRD when the ratio of Fe^{II} and Fe^{III} is small enough. In our experiment, for example, $\alpha\text{-Fe}_2\text{O}_3$ particles are always the only product when $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} < 0.08$ at pH 7 (Fig. 4) and $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} < 0.05$ at pH 9.

The above results lead us to conclude that Fe(II) ions play a catalytic role in the process of phase transformation from ferrihydrite to $\alpha\text{-Fe}_2\text{O}_3$ particles. Preliminary results show that the reaction rate is high enough when $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.02$ in our reaction system (Supporting information). Therefore, $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ usually equals 0.02 in our experiments.

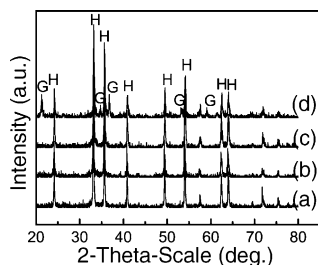


Fig. 4. The XRD patterns of the product at different $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ values at pH 7, (a) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.01$, (b) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.02$, (c) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.07$, (d) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.08$; H, hematite and G, goethite.

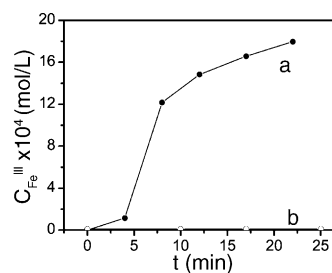


Fig. 5. Changes of the concentration Fe(III) ions in solution with reaction time (a) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.02$, (b) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0$, $C_{\text{total Fe(III)}} = 0.5 \text{ mol/L}$, pH = 7.01.

3.4. The determination of the concentration of Fe(III) ions in solution

According to the published literature data, Fe(II) can catalyze the dissolution of iron(III) (hydro)oxides. In order to understand the action of Fe(II) ions in our system, the concentration Fe(III) ions in solution and the pH value of system at different reaction time in the presence or absence of Fe(II) ions are determined, respectively, by taking subsamples during the reaction. The results are shown in Figs. 5 and 6.

From Fig. 5b, it can be seen that the concentration of Fe(III) ions in solution without Fe(II) is so little that it is below the limit of detection for spectrophotometry. However, the concentration of Fe(III) ions in solution with Fe(II) ions is from 10 to 100 times as high as that without Fe(II) ions. The driving force for Fe(III) desorption lies in the difference in the solubility between ferrihydrite and hematite. When the concentration of Fe(III) ions is saturated for hematite it is unsaturated for ferrihydrite. So, hematite are grown by deposition of the solute originally presence in the solution phase and indirectly furnished from ferrihydrite by dissolution. The action of Fe(II) ions is to accelerate the dissolution of ferrihydrite thereby accelerating the whole phase transformation from ferrihydrite to hematite.

The results in Fig. 2 show that the time for completing the phase transformation from ferrihydrite to hematite is about 22 h in the absence of Fe(II), while it is 0.5 h in the presence of Fe(II). The curve b of Fig. 6 indicates that the pH of the system decreases slowly in the absence of Fe(II) ions, which is consistent with its slow rate of phase transformation at this

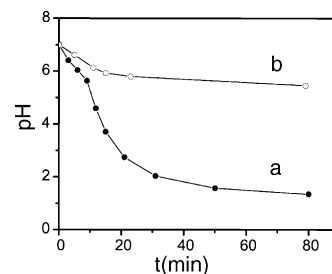


Fig. 6. Changes of pH value of reaction system with reaction time, where all measurements were conducted at room temperature (a) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.02$, (b) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0$, $C_{\text{total Fe(III)}} = 0.5 \text{ mol/L}$, pH = 7.01.

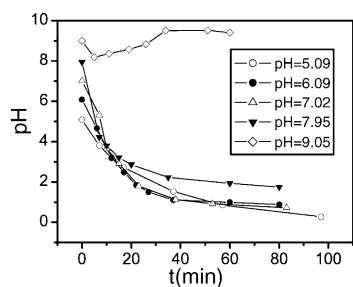


Fig. 7. Changes of pH with reaction time, where all measurements were conducted at room temperature ($C = 0.5 \text{ mol/L}$, $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.02$).

pH. However, the pH value of the system (Fig. 6a) decreases rapidly in the presence of trace amounts of Fe(II) ions, which also coincides with its rapid reaction rate. Further, the changes of pH with the reaction time at various initial pHs in the presence of Fe(II) ions were also determined (Fig. 7).

It is obvious that the change trend of pH with reaction time at pH 9 is different with that at pH 5–8 (Fig. 7). The pH of the system decreases rapidly with the reaction proceeding when the initial pH is 5–8. When the pH is 9, pH value decreases a little with the reaction proceeding at the early stages of the phase transformation and then increases until it reaches a stable value. It is not difficult to deduce that the concentration of Fe(III) in solution in the system of initial pH 9 is so low that it is certainly below the limit of detection for spectrophotometry. The fact, however, is the phase transformation from ferrihydrite to hematite at pH 9 is completed in a very short time (Fig. 2). Obviously, this result cannot be explained by Fe(II) catalyzing the dissolution of ferrihydrite.

3.5. The influence of Na^+ and Cl^- ions

In the reaction process, Na^+ and Cl^- ions are introduced into the system via the synthetic route employed. They have little effect on the purity of the product, because they can be easily eliminated from the product by washing it with distilled water. However, the presence of Na^+ and Cl^- has an effect on the size of hematite particles. According to the literature data [3], the nucleation of hematite takes place within the ferrihydrite aggregate and the amount of Fe in the aggregate determines the final size of the hematite crystal, which is, therefore, related to the aggregate size of the precursor. The preliminary tests show the size of the particles decreases with the increase in the concentration of Na^+ and Cl^- ions. This is probably because high ion strength makes the precursor easily flocculate to be more little aggregate. The more detailed discussion will be reported in another paper on the preparation of hematite particles.

3.6. Discussion about the phase transformation mechanism of ferrihydrite

It is known that ferrihydrite is metastable with regard to goethite and hematite and should spontaneously transform

to these minerals. Increasing temperature or a pH close to the point of zero charge (pzc) of ferrihydrite favors hematite and disfavors goethite [3]. It has been confirmed that lepidocrocite and goethite forms from ferrihydrite by a dissolution/reprecipitation mechanism [15]. As far as hematite concerned, it has been reported that hematite forms by two mechanisms. One is a dissolution/reprecipitation mechanism [2]. The other is a solid-state transformation [15,16].

In fact, lepidocrocite and goethite are obtained in current system when the reaction is carried out at a low temperature. A number of experiments have shown that the higher the reaction temperature is and the higher the proportion of hematite in the product is. Once the temperature reaches 100°C , a pure phase of hematite can be obtained. The result in Fig. 5 indicates the dissolution of ferrihydrite is certainly accelerated due to the presence of Fe(II) and the product is also confirmed to be pure hematite particles at 100°C (Fig. 4). These results lead us to the conclusion that hematite particles can grow through a dissolution/reprecipitation mechanism in current system.

However, it is difficult to explain the result obtained at initial pH 9 by a dissolution/reprecipitation mechanism. It is only explained through a solid-state transformation. In order to confirm this concept, the pzc of ferrihydrite in the current system was determined and its value is 9.2. This result provides further support for the solid-state transformation from ferrihydrite to hematite at pH 9. Based on the literature data [3], the strong hematite favoring effect at pH values close to the pzc of ferrihydrite is most likely associated with its solubility minimum in this pH range. A low solubility suppresses the via-solution formation of goethite, and thereby, favors the transformation to hematite within the ferrihydrite aggregate by a solid-state transformation. In addition, in the solid-state transformation mechanism, nucleation/growth of hematite involves a combination of dehydration and rearrangement processes which are facilitated by the structural resemblance between ferrihydrite and hematite [17], that is to say, they all belong to the hexagonal crystallographic system. The action of Fe(II) is likely to accelerate the nucleation/growth of hematite.

Both dissolution/reprecipitation and solid-state transformation can be explained by electron transfer. The first step is the adsorption of Fe(II) ions. The second step is probably electron transfer between adsorbed Fe(II) and interfacial Fe(III) and this electron transfer is continually repeated. The action of Fe(II) lies in the ability to promote reductive dissolution of ferrihydrite on one hand. On the other hand, its action lies in the ability to promote a solid-state transformation from ferrihydrite to hematite. In our system, it is possible that the two mechanisms coexist in the pH range 5–9. Which mechanism predominates depends on the reaction conditions, such as temperature, initial pH of the system, etc. Because adsorbed Fe(II) is a stronger reducing agent than dissolved Fe(II) [18,19], a low pH disfavors the adsorption of Fe(II) due to the positive charge of the substrate and the action of Fe(II) is not obvious at $\text{pH} < 5$ (Fig. 2). In addition, the phase

transformation from ferrihydrite to hematite at the initial $\text{pH} > 9$ can be completed in a short time in the absence of Fe(II) , so the catalytic action of Fe(II) is also not obvious at $\text{pH} > 9$. Only in the pH range 5–9, Fe(II) can cause a rapid phase transformation from ferrihydrite to hematite.

As is well known, Fe(II) ions exist in different forms at different pH s. It implies that some rather than all species of Fe(II) ions can play a catalytic role. In order to understand which species of Fe(II) ions plays the role to accelerate the phase transformation, the concentrations of different species of Fe(II) ions at different pH should be measured. In fact, this is a rather troublesome work for our system. Fortunately, however, the data measured by Инцирвели et al. [20] may help us to explain the above results. According to the reports of Инцирвели, in pH range from 5 to 9 Fe(II) ions exist in the form of Fe^{2+} , FeOH^+ , Fe(OH)_2 and Fe(OH)_3^- . At pH 5, the species of Fe(II) ions in the system comprise both Fe^{2+} and FeOH^+ , but the concentration of Fe^{2+} ions predominates. At pH 7, the species of Fe(II) are Fe^{2+} , FeOH^+ and Fe(OH)_2 but the concentration of FeOH^+ ions is the largest (about 60%). And at pH 9, the amount of Fe(OH)_2 instead of FeOH^+ and Fe(OH)_3^- predominates. Preliminary test shows that the reaction rate at pH 5 is lower than that at pH 7 or at pH 9 in the presence of Fe(II) . Based on the literature data and our experimental results, we guess that the main species of Fe(II) ions involved in the catalytic action is FeOH^+ and Fe(OH)_2 probably. It is possible that FeOH^+ ions catalyze the dissolution of ferrihydrite leading to the formation of hematite by a dissolution/precipitation process and Fe(OH)_2 accelerate the phase transformation from ferrihydrite to hematite by a solid-state reaction.

It easily can be seen from the data in Fig. 3 that only 26% of Fe(II) ions are adsorbed on the surface of ferrihydrite at pH 5, while more than 90% of Fe(II) ions at pH 7 are adsorbed. So, the amount of Fe(II) ions which actually take the catalytic action in the transformation of ferrihydrite at pH 5 is lower

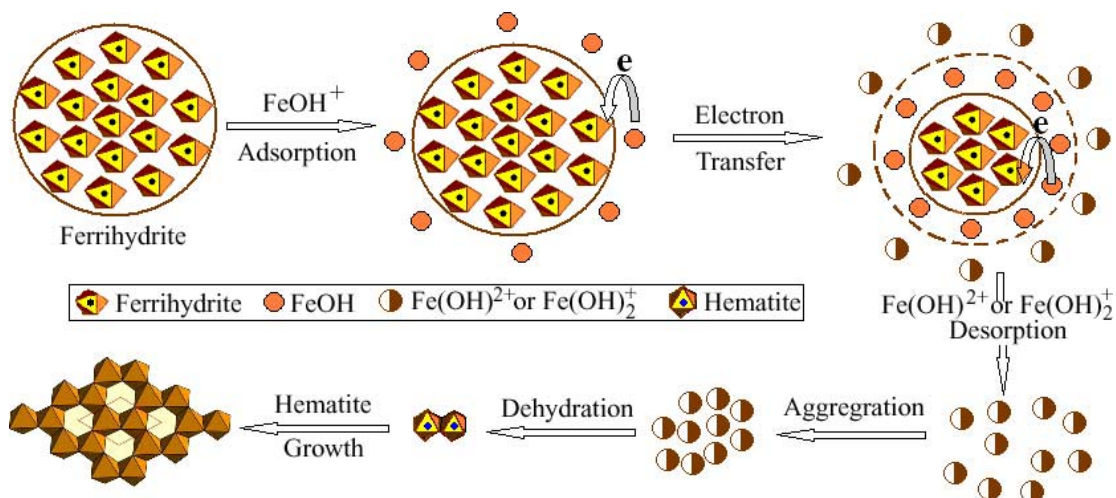
than that at pH 7 though the recovery of Fe(II) ions at pH 5 is higher than the one at pH 7. This observation can be used to explain the reason why the reaction time at pH 5 is longer than that at pH 7.

In the current system, the pzc of ferrihydrite is about 9.2. Though other species of Fe(II) besides Fe(OH)_2 at pH 9 are probably adsorbed on the ferrihydrite, however, the amount of them is so small that it is difficult to understand the fact that the transformation from ferrihydrite to hematite was completed in a so short time. So, it is deduced that the species of Fe(II) taking the catalytic action should be Fe(OH)_2 . In the experimental course, Fe(II) ions were added into the freshly precipitated ferrihydrite system under vigorous stirring. So, probably, Fe(OH)_2 monomers instead of bulk Fe(OH)_2 were adsorbed on the ferrihydrite and accelerate the solid-state transformation from ferrihydrite to hematite. It is coincident that Fe(OH)_2 also belongs to the same crystallographic system as ferrihydrite and hematite, which further supports structurally this catalytic action.

Another evidence for the latter mechanism derives from an experiment conducted at lower initial concentration. The results show that the time needed for completing the phase transformation from ferrihydrite to hematite at pH 9 is much shorter than the time at pH 7 when the initial concentration of ferrihydrite is as low as 0.05 mol/L. When hematite forms by a dissolution/precipitation process (pH 7), a low initial concentration of ferrihydrite leads to a low concentration of Fe(III) ions dissolving into solution so that it needs a long time to reach the saturated concentration to form hematite particles. However, when hematite forms by a solid-state transformation mechanism, a low initial concentration of ferrihydrite has only a less effect on the phase transformation process.

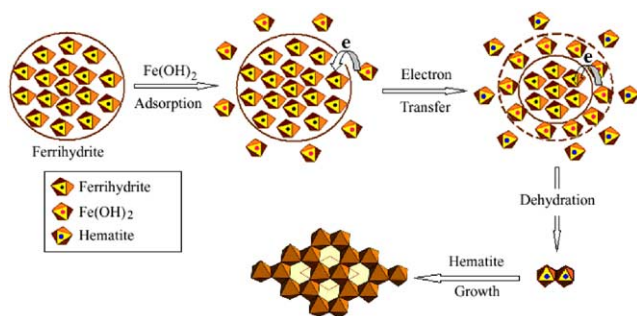
The following diagrammatic sketches may demonstrate the two catalytic mechanisms.

(1) Dissolution/precipitation mechanism



In the dissolution/precipitation mechanism, firstly, FeOH^+ is adsorbed on the surface of ferrihydrite. Then electron transfer between Fe(II) and interfacial Fe(III) takes place and this electron transfer is continually repeated. Thus, the original adsorbed Fe(II) is oxidized to become Fe(III) and to detach from the surface of ferrihydrite into solution. Those Fe(III) exists in solution in form of $\text{Fe}(\text{OH})^{2+}$ or $\text{Fe}(\text{OH})_2^+$ depending on pH of the solution. Subsequently, those Fe(III) ions deposit rapidly to form hematite particles.

(2) Solid-state transformation mechanism



In the solid-state transformation mechanism, the first two steps are still the adsorption of $\text{Fe}(\text{OH})_2$ and electron transfer between Fe(II) and Fe(III). Because $\text{Fe}(\text{OH})_2$, ferrihydrite and hematite share a similar hexagonal close-packed anion sublattice, those oxidized Fe(II) is probably to become directly hexagonal sublattice of Fe(III). Those hexagonal sublattice aggregate and dehydrate to form the primary particles of hematite and then to grow up to be hematite particles.

4. Conclusions

When the pH of a reaction mixture of ferrihydrite and the Fe(II) ion is raised from 5 to 9, the ferrihydrite is transformed rapidly to hematite particles at 100 °C. The transformation is triggered by the adsorption of Fe(II) ions on ferrihydrite at a pH above 5. Except at pH 9, most of Fe(II) ions can be reclaimed at 5–8. Fe(II) is thought as a catalyst for the phase transformation from two-line ferrihydrite to hematite. The adsorption of Fe(II) and electron transfer between Fe(II) and Fe(III) plays a fundamental role in the catalytic phase transformation. In the presence of trace amounts of Fe(II), not only the dissolution of ferrihydrite is accelerated, thereby,

leading to a rapid formation of hematite through a dissolution/precipitation mechanism, but also the solid-state transformation from ferrihydrite to hematite is also accelerated. In the former mechanism, it is possible that Fe(II) in form of FeOH^+ takes the catalytic action, while $\text{Fe}(\text{OH})_2$ is a catalyst for the phase transformation of ferrihydrite in the latter mechanism. The relative importance of the two pathways depends on the reaction conditions, such as temperature and pH.

Appendix A. Supporting information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2004.09.019.

References

- [1] S. Music, A. Vertes, G.W. Simmons, I. Czako-Nagy, H. Leidheiser, *J. Colloid Interface Sci.* 85 (1982) 256.
- [2] T. Sugimoto, K. Sakata, T. Muramatsu, *J. Colloid Interface Sci.* 159 (1993) 372.
- [3] U. Schwertmann, J. Friedl, H. Stanjek, *J. Colloid Interface Sci.* 209 (1999) 215.
- [4] R. Comell, R. Giovanolli, W. Schneider, *J. Chem. Technol. Biotechnol.* 46 (1989) 115.
- [5] W.R. Fisher, U. Schwertmann, *Clays Clay Miner.* 23 (1975) 33.
- [6] R.M. Cornell, *Z. Pflanzenernahr. Bodenk.* 150 (1987) 304.
- [7] R.M. Cornell, R. Giovanolli, W. Schneider, *Clay Miner.* 38 (1990) 21.
- [8] B. Wehri, B. Sulzberger, W. Stumm, *Chem. Geol.* 78 (1989) 167.
- [9] E. Tronc, P. Belleville, J.P. Jolivet, *J. Livage Langmuir* 8 (1992) 313.
- [10] J.P. Jolivet, P. Belleville, E. Tronc, *J. Livage Clays Clay Miner.* 5 (1992) 531.
- [11] Wuhan University Compilation Group, *Experiment of Analytical Chemistry*, High Education Publishing Company, Beijing, 1987, 354.
- [12] J.M. Combes, A. Manceau, G. Calas, J.Y. Bottero, *Geochim. Cosmochim. Acta* 53 (1989) 583.
- [13] V.A. Drits, B.A. Sakharov, A.L. Salyn, A. Manceau, *Clay Miner.* 28 (1993) 209.
- [14] W. Feitknecht, W. Michaelis, *Helv. Chim. Acta* 45 (1962) 212.
- [15] R.M. Cornell, W. Schneider, *Polyhedron* 8 (1989) 2829.
- [16] D. Andreeva, I. Mitov, T. Tabakova, V. Mitrov, A. Andreev, *Mater. Chem. Phys.* 41 (1995) 146.
- [17] R.M. Cornell, U. Schwertmann, *The Iron Oxides*, VCH Publishers, New York, 1996, 323.
- [18] W. Stumm, B. Sulzberger, *Geochim. Cosmochim. Acta* 56 (1992) 3233.
- [19] E. Liger, L. Charlet, P. Van Cappellen, *Geochim. Cosmochim. Acta* 63 (1999) 2939.
- [20] Л.И. Инцкирвели, И.В. Колосов, Г.М. Варшал, Ж. Неорг. Хим, 20 (1975) 2388.